2.1.   Applicant notes that the restriction requirement between the claims of Group I (Claims 10-19, drawn to a method) and Group II (claims 20-27 drawn to a catalyst), which was made final in the office action of 3 August 1999 has apparently been taken as accepted by the Applicants; this is by no means so even though no petition was filed from the requirement. Instead, the prosecution of the claims in question was carried forward into the CPA on which this is the first action. Applicant submits, in response to the Examiner's statement in Paper No. 9, (page 2) that it is not incumbent on the Applicant to provide evidence in support of a proposition (here, that the claims are directed to separate and distinct inventions) but rather, the Examiner, who is required to support agency action by substantial evidence made of record in the proceedings.

2.2   The Patent and Trademark Office is an "agency" subject to the constraints of the Administrative Procedure Act (APA), as established by the Supreme Court decision in *In re Zurko*, 50 USPQ 2d 1930. Here, the conclusion that the claims are directed to separate and different inventions, with its consequent refusal to examine them (and potentially, the imposition of a further and separate application in order to obtain a patent for the claims in question) constitutes "agency action" and a reviewing court would apply the APA's court/agency review standards in the absence of an exception. The Examiner's action is therefore subject to the requirements of the Act which include the requirement that the action be supported by substantial evidence. The agency decision here would be subject to judicial review under Section 706 of the Act. This section, originally enacted in 1946, sets forth standards that govern the scope of court "review" of agency action. It states that a reviewing court shall--

> "(2) hold unlawful and set aside agency . . . findings . . . found to be --
>
> (E) *unsupported by substantial evidence* in a case subject to sections 556 and 557 of this title or *otherwise reviewed on the record of an agency hearing provided by statute*; . . ." (Emphasis added)

2.3.   Here, there is no substantial evidence in the present record which shows that the claimed catalyst can be used in any different process or, at least, in any different process with any expectation of a useful result, as asserted by the Examiner.   Since, therefore,

there is nothing to warrant the Examiner's speculation, it is submitted that adherence to the regulatory prescription should be determined by the evidence of record rather than on the mere assertion. There is no evidence to support the Examiner's restriction requirement and it should therefore be withdrawn. It is not for the Applicant to support a case of the unitary character of the invention by adducing evidence to this effect but rather, the Examiner who is given the burden by the Act, of supporting the agency action by substantial evidence.

2.4. The Office cannot have it both ways, it cannot have its cake and eat it, it cannot have the judicial deference prescribed by the APA and not adhere to the substantiation requirements of the APA. If the Office wishes - as devoutly as it did in the *Zurko* case - to have the APA apply to its proceedings, it must accept, following its success before the courts, that the APA applies to all aspects of its proceedings, including this one. It is not the burden of the Applicant to show "the proposed alternate use cannot be accomplished" but rather, the Examiner who is under the burden of supporting the conclusion of inventive separateness and distinctiveness by substantial evidence of record. It is submitted that a single sentence in a letter (Paper No. 5) does not provide anything beyond a wholly unsubstantiated, utterly speculative assertion of the matter stated. There is not even a scintilla of evidence to support the assertion and certainly not the substantial evidence required to support a conclusion of this agency. See *Universal Camera Corp. v. NLRB* 340 U.S. 474 (1951), *Washington V.&M. v. Coach Co. v. Labor Board* 301 U.S. 142, *Labor Board v. Columbian Enameling and Stamping Co.* 306 U.S. 292, 300. To be specific, there is not even any reference to a published scientific document which might permit an inference properly to be drawn that the matter stated is so. Applicant's attorney apprehends that if he were to make any similarly unsubstantiated assertion on a contested matter, the Examiner would give it short shrift without any qualms.

2.5. Here, the Examiner has stated that the product claimed can be used in a materially different process "such as in a molecular sieve" (Paper No. 5, page 2). The significance of this statement is not fully clear to Applicant since, in the first place a molecular sieve is not a process. Clarification appears necessary. Second, it is submitted that any alternative use should be one which is substantial and which relates to the inventive properties of the product. Obviously some other uses will always be to hand, for example, the product could

be used as a low density aggregate for concrete or as landfill but, if the Examiner should seek to assert such uses for the product, Applicant will take the position that such trivial utilizations are not the type of alternative uses of which the Office may take cognizance in the determination of inventive character. The only uses which might be contemplated as providing any reasonable basis for the conclusion of inventive distinctness are those which rely upon the same properties of the product as are utilized in the inventive process. The Examiner has not shown that any such utility is reasonably to be expected of the present products and accordingly, the conclusion of inventive distinctness and the restriction requirement based upon it must be withdrawn.

3.   The abstract and the specification have been amended in order to identify correctly the period in the Periodic Table that is being referred to in the specification. As filed, the specification stated that the preferred base metals were selected from Period 3 of the Table, with vanadium, iron, cobalt, zinc and gallium being effective and vanadium being the most preferred metal component (page 10, line 28). The reference to Period 3 was intended to cover these metals but was incorrect: these metals belong in Period 4, as shown by the attached references:

> "Chemistry of the Elements" Greenwood and Earnshaw, Pergamon Press, 1986.
> "Advanced Inorganic Chemistry" Cotton and Wilkinson, John Wiley & Sons, 1980.

Since it is in the public interest to have the specification in scientifically correct form, correction of this error is requested.

4.   Claims 1 and 11 have been amended to specify that the metal component of the sulfur reduction catalyst is a non-lanthanide. None of the metal components described in the specification are members of the lanthanide series and the change is desirable for this reason alone; in addition, it assists in delimiting the scope of the catalyst from the well-known and established use of rare earths (of the lanthanide series) in zeolitic cracking catalysts. See, for example, Fluid Catalytic Cracking with Zeolite Catalysts, Venuto and Habib, Marcel Dekker Inc., New York 1979, ISBN 0-82470-6870-1, page 32 (copy attached).

5.1.   The Examiner has rejected claims 1-7 and 10 under 35 U.S.C. 102(b) or 35 U.S.C. 103(a) as obvious over the disclosure in Collins, et al. U.S. 5,482,617; claims 11-14, 17-9 and 28-31 have been rejected as unpatentable over Collins under 35 USC 103(a). These rejections may conveniently be discussed together.

5.2.   As the Examiner has noted, Collins deals with a desulfurization process for a catalytically cracked feed stream which may be derived from an FCC process (Paper no. 5, page 6). In the Collins process, the low boiling range feed which contains organic sulfur compounds is contacted with a catalyst in a fixed fluidized bed at elevated temperatures in the range of 700 to 850°F (column 2, line 30-36; column 4, lines 4-5. The desulfurized product is a gasoline range material, as noted at column 5, line 2. The catalyst used in the Collins process is an acidic zeolite such as ZSM-5 (intermediate pore size), or zeolite Y or zeolite beta (both large pore size materials). These zeolites may be employed in their acid forms or iron exchanged or impregnated with one or more suitable metals including zinc, nickel, cobalt and metals of other groups of the Periodic Table (column 5, line 29-42).

5.3.1. Two principal distinctions may be noted between the Collins process and the present catalytic cracking method. First, Collins uses a low boiling range feed which is distinct from the heavy oil feed used in the catalytic cracking process of the present invention. As the Examiner has noted (Paper No. 5, page 6), the Collins feed is a catalytically cracked feed stream derived from an FCC process; in other words, it is the *product* of a catalytic cracking process rather than the heavy oil *feed* which goes into a catalytically cracking process. Examples of feeds which may be used in the Collins process include catalytically cracked naphthas, pyrolysis gasoline, coker gasoline, FCC gasoline, reformate and thermally cracked pyrolysis and/or coker fractions (column 2, lines 37-47). Examples in the specification include naphtha and a heart-cut reformate with an end point of 190°F (88°C). The highest boiling point encountered in the examples is the 430°F (221°C) for the full range FCC naphtha (Table 4, Example 6).

5.3.2. The Examiner's argument that "the references disclosure of a feed containing olefins and aromatics such as a reformate is considered to encompass applicant's heavy feed" (Paper No. 17, page 4) is misplaced.   Reformates are not heavy materials comparable to

applicant's gas oil feeds (note especially claims 28 and 31); by contrast, they are generally considered to be low boiling fractions in the gasoline range, as shown by the attached copy of *Modern Petroleum Technology*, G. D. Hobson (Ed.), Applied Science Publishers, 1973, ISBN 0-85334-487-6, page 333, which states that the end point of the feed to the reformer is typically limited to about 190°C (374°F) with an end point increase of 15°C taking place during processing. *Petroleum Processing*, Hengstebeck, McGraw Hill, 1959, page 192, 193. See also U.S. 5,520,798 column 1, lines 8-12; column 3, lines 43-54, especially line 44 (feeds in the gasoline boiling range); Example II (feed is C_6-C_7 naphtha). As to the presence of olefins and aromatics, this is not a relevant factor in considering the boiling range of the feed. Both olefins and aromatics may have varying boiling temperatures, depending on molecular weight and composition, so that the references in Collins to olefins and aromatics are merely expressions of chemical composition rather than physical parameters, of the chemical character of the feed rather than its boiling point. What is important in the Collins description of the feeds is that Collins does not describe the use of heavy feeds comparable to Applicants feeds such as gas oil in his process. Collins discloses only lower boiling feeds.

5.3.3. The Examiner has stated (Paper No. 17, pages 7 – 8) that according to Collins, "the feed can be derived from thermally cracked pyrolyis and coker fractions" (presumably a reference to the disclosure at column 2, lines 42-44 and column 3, lines 29-31). The first point that Applicant would make to this assertion is that derivation does not imply character. The fact that a feed may be derived from a given material does not mean that the feed takes of the essential nature of that material. Common salt, for example, is *derived* from chlorine, a poisonous gas and sodium a metal which reacts violently with water but salt, by contrast, dissolves readily in water and is required for physiological health. Here, Collins states that heavier olefins, if present, are generally obtained from cracking processes (column 2, lines 42-44; column 3, lines 16-18). These materials, however, remain distinct from the heavy oil feeds such as those used in the present process which are themselves, the materials subjected to cracking as distinct from the products of the cracking (by definition, lower molecular weight, lower boiling fractions) mentioned by Collins. There is, in particular, nothing in Collins which suggests that a gas oil feed might be used.

5.3.4. For these reasons alone, the rejection based on Collins should be withdrawn, especially with respect to claims 28 and 30.

5.4.1. A further distinction is this, as previously noted: the Collins process is not a catalytic cracking process. This is made clear by the disclosure in Collins which states the following:

> The reactor and regenerator operating temperatures are mild compared to FCC conditions. Expensive alloys or refractory linings are not required in the design. Operating pressure is designed to be compatible with existing FCC unsaturated gas plant pressure. Direct transfer of FCC offgas to the unit of the present invention is preferred, avoiding the added cost of a compressor. FCC offgas needs only to go through a fuel gas amine contactor to remove hydrogen sulfide. (Column 7, lines 1-9).

Reference to the Examples shows that the typical range of temperatures encountered in the Collins process is 750 to 850°F (400 to 455°C) which is below the range of temperatures encountered in catalytic cracking operations.

5.4.2. The Examiner has not taken this point, stating that the reference similarly discloses contacting the feed with a catalyst at "elevated temperatures" which would accomplish cracking because the same feed is contacted with the same catalyst under the same elevated conditions" (Paper No. 17, page 8). First, as noted above, Collins does not describe the same feeds; Collins feeds are light, Applicant's feeds are heavy. Second, if the Collins disclosure itself draws a distinction between its conditions and those of FCC, it is, to say the least, disappointing that the Examiner should give no weight to that fact. Reference to the actual data in Collins supports the self-characterization of the process, the highest temperature used is 850°F (Example 6). Note also in Example 6 that the "Full Range FCC" feed here had an T_{99} point of 430°F, indicating that it was a cracked feed rather than a feed for cracking, again providing support for the proposition that the Collins process is not an FCC process as claimed in claims 11 to 19, 30 and 31 at least.

5.4.3. It is submitted that the claims as filed adequately distinguish the present process from the disclosure in the Collins reference since both claims 1 and 11 specifically refer to the operation as being one of catalytic cracking, thereby implying all the conditions and parameters appropriate to that process which, as Collins points out, is *not* a process of the

kind disclosed in that reference. Further, both claims 1 and 11 refer to the fact that the feed is subjected to cracking and that the product of the process included cracking products. None of these features are found in Collins which, as just noted, does not describe a catalytic cracking process. Furthermore, note that claim 11 refers to the use of a heavy hydrocarbon feed in a process which is defined as having the features of the FCc process which Collins emphatically does not teach, again emphasizing the distinction.

5.5.   Further distinction over the Collins disclosure is that Collins refers specifically to the use of only certain metal components none of which is vanadium or iron, two of the preferred metals used in the present catalytic materials. For this reason, claims 32 to 35 at least, are patentable over Collins.

5.6.   With respect to the obviousness rejection of claims 11-14, 17–9 and 28-31, the Examiner has acknowledged the existence of three differences between the prior art and the claimed invention:

1.   The use of a VGO feed
2.   The specific catalyst regeneration steps.
3.   The use of a riser reactor apparatus.

5.6.2   With respect to the use of the VGO feed, the Examiner has stated that "it would have been obvious to one of ordinary skill in the art at the time the invention was made to treat any hydrocarbon stream containing unwanted organic sulfur compounds according to the Collins et al (5,482,617) process, including applicant's specific gas oil because the reference of Collins et al (5,482,617) does not limit the specific organic sulfur compounds treated" (Paper No. 17, page 7). So, it seems that prior art is now to be interpreted to mean that anything not specifically precluded by the terms of the prior art reference is to be considered as within the scope of the prior art. A truly extravagant proposition that seems to be unsupported by any legal precedent. The point is that a proper interpretation of the prior art is that it includes just what it says and nothing more – it does not extend out into some indefinite continuum limited only by the Examiner's needs and imagination. The question of obviousness however, may take a broader view of the matter but it still does not

permit all the confines of the historical disclosures to be blithely cast aside. The Examiner is not free to assert that "it would have been obvious ... to treat any hydrocarbon stream containing unwanted organic sulfur compounds according to the Collins et al (5,482,617) process" solely because the reference "does not limit the specific organic sulfur compounds treated". It is not obvious for the reason stated: the prior art is not to be stretched out simply on the grounds that it does not preclude what is now claimed. The analysis that the Examiner is required to make is to determine the content and scope of the prior, to determine the skill and level within the art and then to make the determination of obviousness – and the content of the prior art does not include everything (now conveniently aided by copious amounts of hindsight) that is not expressly excluded by the terms of the art.

5.6.3   What Collins does disclose is the use of certain low boiling feeds (see 5.3.1 above) and this must provide the starting point for the analysis of the art. Collins does not suggest (and neither does any other reference of record) that his process would be applicable to any "hydrocarbon stream containing unwanted organic sulfur compounds"; in fact, Collins is quite restrained in his teachings and provides no basis for any reasoned suggestion that the same process would be applicable to heavier feeds. And there would be good reason why a skilled person would not consider the Collins process to be applicable to heavier feeds. Heavier feeds contain more aromatics and have a higher Conradsen Carbon Number (CCR); they tend on catalytic cracking to produce more coke which is deposited on the catalyst and which deactivates it. Now, Collins process is a dense, i.e. fixed, fluidized bed process (column 6, lines 52-55) from which only a slipstream of catalyst is removed for regeneration (column 6, line 60); this implies that the catalyst is to be one which has an extended period of activity in the bed: the catalyst is not regenerated upon each cracking cycle as in the FCC process. Heavier feeds, however, would be expected to deactivate the catalyst more quickly to the point that they would render the catalyst inactive and the process as a whole inoperable. Thus, Collins does not suggest the possibility- far less the desirability of using "any hydrocarbon stream containing unwanted organic sulfur compounds". The Examiner's proposition is as technically flawed as it is legally deficient.

5.6.4. Second, with respect to the specific catalyst regeneration steps, the Examiner's position is similar: because Collins does not "limit the specific regeneration steps", any regeneration must be obvious. Again, Applicant points out the lack of any precedential support for this proposition. And yet again, it is technically flawed. The Collins regeneration process using a slipstream (withdrawal of part of the catalyst from the bed) and this is because the Collins process operates, as noted above with a low boiling stream which enables catalyst activity to be maintained over an extended duration. Regardless of how conventional Applicant's regeneration steps might be in the context of the FCC process, they have not been shown by the record to be ones which would commend themselves as the ones of choice in the Collins process that is, the ones which should be used in that process. The test of obviousness is of desirability not mere possibility (see, for example, *In re Gordon* 221 USPQ 1125, 1127 (Fed. Cir. 1984). *In re Deminski* 230 USPQ 313, 315 (Fed. Cir. 1986). *In re Laskowski* 10 USPQ 2d 1397, 1398 (Fed. Cir. 1989). *In re Geiger* 2 USPQ 2d 1276, 1278 (Fed. Cir. 1987). The limits of obviousness based on the prior art are not set by what the art expressly excludes but rather, but what the skilled person would infer from that art and what the skilled person would consider desirable to do in the light of the art. Nothing here indicates why the skilled person would have sought to apply the regeneration steps of the conventional FCC process to the Collins process which characterizes itself as different from that process.

5.6.5. As far as the riser reactor is concerned, the Examiner dismisses the significance of the limitations to the use of the riser reactor on the basis that "invention in a method must be found in the steps performed and not the apparatus employed". Whatever the merits of the decision in *Ex parte Hart*, precedent does not create fact and here, the fact remains that the riser FCC process is recognized in the art as one which is a process or method carried out in apparatus specifically adapted to that process; the process and its apparatus are inseparable – FCC cannot be carried out in a test tube or in a beaker. The Examiner's reliance on some hoary legal precedent is therefore misplaced and to the extend that the conclusion of obviousness is based on this consideration, it should be withdrawn.

5.7. In more general terms, it is believed that the present claims are not obvious in view of Collins because there is nothing in Collins which indicates that its prescriptions would be

applicable to the more severe conditions encountered in catalytic cracking operations and with the heavy oil feeds characteristic of catalytic cracking. Specifically, the organic sulfur compounds which are present in the high boiling feeds typically used in FCC e.g. vacuum gas oil, contain the sulfur in the form of benzothiophenes, dibenzothiophenes and alkylated benzothiophenes which are more resistant to removal than the mercaptans and simple thiophenes present in the low boiling feeds such as those noted in Collins. Given that this refractory character of the sulfur compound in FCC feeds is well known, there is no reason why a skilled person would have thought that it would have been desirable to extend any potential of the Collins for desulfurization activity to the more severe conditions encountered in FCC with more refractory feeds. The present claims are therefore believed to be unobvious and therefore patentable over the Collins disclosure.
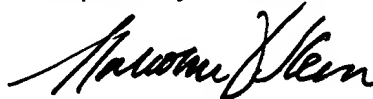
6.   The second rejection under 35 USC 103 is based on the Collins and Chu references. Chu is relied on, in addition to Collins, to support the proposition that the choices of alpha values and unit cell sizes for the molecular sieve (claims 8, 9, 15 and 16) are do not render these claims patentable. Applicant considers that these claims are patentable over the Collins and Chu teachings for the reasons advanced above with respect to Collins. In order to facilitate consideration of the real issues in this case, Applicant will not at the present time advance further arguments with respect to the rejection based on the combined Collins/Chu references but will rely upon the arguments set out above given with respect to Collins.

7.   In view of the remarks and amendments set out above, reconsideration and withdrawal of the objections and rejections is requested.

Respectfully submitted,

December 15, 2000

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Periodic Table of the Elements

Period	Group Ia	Group IIa	Group IIIa	Group IVa	Group Va	Group VIa	Group VIIa	Group VIII			Group Ib	Group IIb	Group IIIb	Group IVb	Group Vb	Group VIb	Group VIIb	Group O
1 1s	1 H																1 H	2 He
2 2s2p	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3 3s3p	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4 4s3d 4p	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5 5s4d 5p	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6 6s (4f) 5d 6p	55 Cs	56 Ba	57* La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7 7s (5f) 6d	87 Fr	88 Ra	89** Ac															

*Lanthanide series 4f

58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu

**Actinide series 5f

90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

Aluminum
Antimony
Argon
Arsenic
Barium
Beryllium
Bismuth
Boron
Bromine
Cadmium
Calcium
Carbon
Cerium
Cesium
Chlorine
Chromium
C balt
Copper
Dysprosium
Erbium
Europium
Fluorine
Gadolinium
Gallium
Germanium
G ld
Hafnium
Helium
Holmium

[a] Elements in
[b] Variation in
[c] Variations
[d] Most comm
[e] A coulometr

Periodic Table of the Elements
and ground-state electronic configurations
(see inside back-cover for Table of Atomic Weights)

Period	IA	IIA		IIIA	IVA	VA	VIA	VIIA	← VIII →			IB	IIB	IIIB	IVB	VB	VIB	VIIB	0
1	1 H $1s^1$		2 He $1s^2$																
2	3 Li [He]$2s^1$	4 Be [He]$2s^2$												5 B $2s^22p^1$	6 C $2s^22p^2$	7 N $2s^22p^3$	8 O $2s^22p^4$	9 F $2s^22p^5$	10 Ne $2s^22p^6$
3	11 Na [Ne]$3s^1$	12 Mg [Ne]$3s^2$												13 Al $3s^23p^1$	14 Si $3s^23p^2$	15 P $3s^23p^3$	16 S $3s^23p^4$	17 Cl $3s^23p^5$	18 Ar $3s^23p^6$
4	19 K [Ar]$4s^1$	20 Ca [Ar]$4s^2$	21 Sc $3d^14s^2$	22 Ti $3d^24s^2$	23 V $3d^34s^2$	24 Cr $3d^54s^1$	25 Mn $3d^54s^2$	26 Fe $3d^64s^2$	27 Co $3d^74s^2$	28 Ni $3d^84s^2$	29 Cu $3d^{10}4s^1$	30 Zn $3d^{10}4s^2$	31 Ga $4s^24p^1$	32 Ge $4s^24p^2$	33 As $4s^24p^3$	34 Se $4s^24p^4$	35 Br $4s^24p^5$	36 Kr $4s^24p^6$
5	37 Rb [Kr]$5s^1$	38 Sr [Kr]$5s^2$	39 Y $4d^15s^2$	40 Zr $4d^25s^2$	41 Nb $4d^45s^1$	42 Mo $4d^55s^1$	43 Tc $4d^55s^2$	44 Ru $4d^75s^1$	45 Rh $4d^85s^1$	46 Pd $4d^{10}$	47 Ag $4d^{10}5s^1$	48 Cd $4d^{10}5s^2$	49 In $5s^25p^1$	50 Sn $5s^25p^2$	51 Sb $5s^25p^3$	52 Te $5s^25p^4$	53 I $5s^25p^5$	54 Xe $5s^25p^6$
6	55 Cs [Xe]$6s^1$	56 Ba [Xe]$6s^2$	57 La* $5d^16s^2$	72 Hf $5d^26s^2$	73 Ta $5d^36s^2$	74 W $5d^46s^2$	75 Re $5d^56s^2$	76 Os $5d^66s^2$	77 Ir $5d^76s^2$	78 Pt $5d^96s^1$	79 Au $5d^{10}6s^1$	80 Hg $5d^{10}6s^2$	81 Tl $6s^26p^1$	82 Pb $6s^26p^2$	83 Bi $6s^26p^3$	84 Po $6s^26p^4$	85 At $6s^26p^5$	86 Rn $6s^26p^6$
7	87 Fr [Rn]$7s^1$	88 Ra [Rn]$7s^2$	89 Ac† $6d^17s^2$	104 Unq	105 Unp	106 Unh	107 Uns											

*	58 Ce $4f^15d^16s^2$	59 Pr $4f^36s^2$	60 Nd $4f^46s^2$	61 Pm $4f^56s^2$	62 Sm $4f^66s^2$	63 Eu $4f^76s^2$	64 Gd $4f^75d^16s^2$	65 Tb $4f^96s^2$	66 Dy $4f^{10}6s^2$	67 Ho $4f^{11}6s^2$	68 Er $4f^{12}6s^2$	69 Tm $4f^{13}6s^2$	70 Yb $4f^{14}6s^2$	71 Lu $4f^{14}5d^16s^2$
†	90 Th $6d^27s^2$	91 Pa $5f^26d^17s^2$	92 U $5f^36d^17s^2$	93 Np $5f^46d^17s^2$	94 Pu $5f^67s^2$	95 Am $5f^77s^2$	96 Cm $5f^76d^17s^2$	97 Bk $5f^86d^17s^2$	98 Cf $5f^{10}7s^2$	99 Es $5f^{11}7s^2$	100 Fm $5f^{12}7s^2$	101 Md $5f^{13}7s^2$	102 No $5f^{14}7s^2$	103 Lr $5f^{14}6d^17s^2$

**† The ground-state configurations for some lanthanide and actinide elements are uncertain

STRIES

and Text Books

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7homas Habib, Jr.

Preparation

Fluid Catalytic Cracking
with Zeolite Catalysts

PAUL B. VENUTO
and E. THOMAS HABIB, JR.
Mobil Research and Development Corporation
Field Research Laboratory
Dallas, Texas

dispersion), are heated at a given temperature for a time period specified to give maximum purity of the desired structure. Approximate conditions for the preparation of synthetic faujasite X are shown in Fig. 13 [15, 16, 181]. As initially crystallized, most zeolites contain sodium cations and are in the form of finely divided particles, on the order of 1 to 7 μm [13, 101, 156, 185]. Excellent overviews of the complex area of zeolite synthesis have been published by Breck [183] and Flanigen [184].

In the next phase the preponderance of sodium may be removed by cation exchange with a medium containing rare-earth cations, or rare-earth cations plus hydrogen ion, or a cation such as ammonium ion capable of conversion to hydrogen ion [13, 17, 18, 127, 156-161]. Inexpensive rare-earth sources (as monazite or bastnasite sands), generally as the chloride salts, are utilized [13, 156-161, 181]; these are rich in cerium, lanthanum, neodymium, and praseodymium, with lesser amounts of samarium, gadolinium, etc. [181]. Comprehensive reviews on zeolitic ion exchange have been published by Sherry [186, 187].

Finally, a siliceous inorganic oxide-type sol or gel (ultimately the matrix) is produced by methods well known in the art [188] (concisely described in a review by Oblad [13]), into which the micron-sized zeolite powder is uniformly dispersed [156, 161], producing a mechanically stable, rugged, microspheroidal composite fluid catalyst after spray drying. Current commercial manufacturing practices vary widely, of course [13].

C. Some Key Structural Features of Zeolites

The structure of zeolites (particularly rare-earth exchanged synthetic faujasites) has been discussed intensively in the literature in relation to their role in catalytic cracking [13, 17, 18, 62, 65, 76, 101, 106, 127, 131, 181, 189, 190]. Particularly relevant are overviews by Ciapetta [191], Meier and Olson [192], Oblad [13], Rabo and Poutsma [193], Smith [194], Turkevich and Ono [195], Venuto and Landis [196], and Weisz [197]. Salient features are summarized below.

Zeolites may be viewed as crystalline, inorganic polymers comprising an anionic lattice of AlO_4 and SiO_4 tetrahedra linked by shared oxygen (Fig. 14). A cubo-octahedron or sodalite cage (Fig. 15A) (24 Al, Si ions, 36 oxygen anions, 8 hexagonal, and 6 square faces) represents the simplest structural building block. When sodalite units are joined in tetrahedral mode (Fig. 16B) (by bridging oxygens across the hexagonal faces), a rigid, three-dimensional reticulum—the faujasite structure (Fig. 16A)—is generated, which upon dehydration

MODERN PETROLEUM TECHNOLOGY

4th Edition

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APPLIED SCIENCE PUBLISHERS LTD

on behalf of

THE INSTITUTE OF PETROLEUM,

GREAT BRITAIN

APPLIED SCIENCE PUBLISHERS LTD
RIPPLE ROAD, BARKING, ESSEX, ENGLAND

The symbol I.P. on this book implies that the text has been officially
accepted as authoritative by the Institute of Petroleum, Great Britain

ISBN: 085334 487 6

WITH 306 ILLUSTRATIONS AND 170 TABLES

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Reprinted 1975

s at high conversion, moving-
but few units were built. The
ontaining hydrogen at approx.
generation side were consider-
lopment appears to have been
Hydroformer at Whiting in an

s based on a platinum–alumina
esigned to give long on-stream
of platinum resulted in a rush
over the following few years.
one, arriving at long on-stream
essing and regeneration periods
orming. Table XXIII lists the

cesses

	Date process announced
ed by	
ment Co	
Standard Oil Co	1939
Co	Mar. 1949
	Feb. 1951
	May 1951
o, Inc.	May 1951
ment Co and	May 1951
ornia	Feb. 1952
lair Refining Co	May 1953
	July 1953
ana)	Nov. 1953
o Inc.	Jan. 1954
s Co	Mar. 1955
	Mar. 1955
gineering Co	Mar. 1956
d Chemicals Corp.	Feb. 1965
	May 1969

that of coke formation. In the
n partial pressure (high plant
nhibit coke formation, whereas
allows for coke formation by
neration. As mentioned pre-
ics is reduced at high pressure,
more hydrocracking must be
production at high pressure.
e conditions is shown in Table
drocracking results in a lower
er C_2–C_4 yield. The regenera-

tive type process, however, needs spare reactors and complicated pipework for switching reactors and regenerating the catalyst.

TABLE XXIV

Comparison of Continuous and R generativ Catalytic R formers

Feed, Kuwait naphtha

Sp gr, 15/15° C		0·763
ASTM distillation, °C		
IBP		115
10% vol		139
50% vol		154
90% vol		169
FBP		179
Naphthenes, % vol		19·4
Aromatics, % vol		15·5
Paraffins, % vol		65·1

	500 psig continuous	200 psig regenerative
Operation		
Yields, % wt		
Hydrogen	1·0	1·9
Methane	2·2	1·1
Ethane	4·5	2·4
Propane	7·2	3·4
Butanes	5·8	3·5
Gasoline	79·3	87·7
Gasoline, ON, Research	95·0	95·0

Feedstocks

Catalytic reformer feeds are saturated (*i.e.* not olefinic) materials boiling up to a maximum of about 190° C. In the majority of cases the feed will be a straight-run naphtha, but other by-product low-octane naphthas (*e.g.* coker naphtha) may be processed after treatment to remove olefins and other contaminants. Hydro-cracker naphtha that contains substantial quantities of naphthenes is also a suit-able feed. It is not usual to include C_5 in the cat. reformer feed as the only reaction capable of giving increased octane number is isomerization, and the equilibrium ratio at reaction temperatures does not give any great improvement. In addition, the hydrocracking reaction breaks C_5 wholly into fuel gas ($C_2 + C_3$ or $C_1 + C_4$), and thus reduces the yield of gasoline on feed.

The yield of gasoline of a given octane number and at given operating condi-tions depends on the hydrocarbon type analysis of the feed, high naphthene stocks, which readily give high aromatic gasolines, are the easiest to reform and give the highest gasoline yields. Paraffinic stocks, however, which depend on the more difficult isomerization, dehydrocyclization and hydrocracking reactions, require more severe conditions and give lower gasoline yields than do the naphthenic stocks. The difference becomes more marked at high octane numbers (Fig 37).

The end point of the feed is usually limited to about 190° C, partially because of increased coke deposition on the catalyst as the end point increases and partially because there is an increase in end point during processing of some 15° C. Limiting the feed end point avoids a redistillation of the product to meet the normal gasoline end-point specification of 205° C maximum.
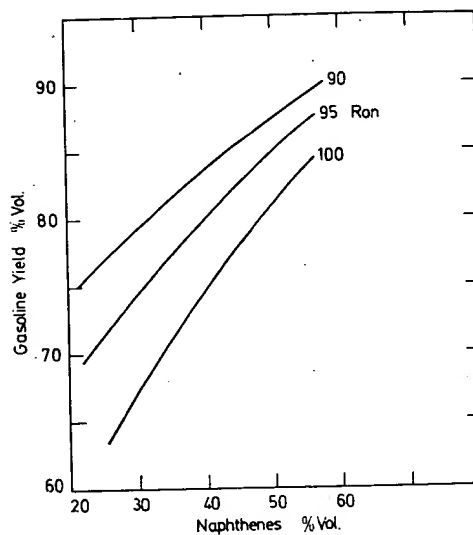
FIG 37. Gasoline yields.

Platinum is easily poisoned, and it is therefore necessary to exercise very careful control over contaminants in the feed to a catalytic reformer, the most important being as follows:

Sulphur

Under the high hydrogen partial pressure conditions used in catalytic reforming, sulphur compounds are readily converted into hydrogen sulphide, which, unless removed, will build up to a high concentration in the recycle gas. Hydrogen sulphide is a reversible poison for platinum, and causes a decrease in the catalyst dehydrogenation and dehydrocyclization activities. In the first catalytic reformers the hydrogen sulphide was removed from the gas recycle stream by absorption in, for example, diethanolamine. Modern units usually remove the sulphur from the feed by conventional desulphurization over cobalt-molybdenum catalyst. An additional benefit of desulphurization of the feed to a level of <5 ppm sulphur is the elimination of H_2S-corrosion problems in the heaters and reactors.

Nitrogen

Organic nitrogen compounds are converted into ammonia under reforming conditions, and this neutralizes acid sites on the catalyst and thus represses the activity for isomerization, hydrocracking and dehydrocyclization reactions. Very small quantities (1–2 ppm) can have an adverse effect. Normally, straight-run materials do not present serious problems with regard to nitrogen, but feeds such as coker naphtha may contain around 50 ppm nitrogen. Removal of this quantity may require high pressure hydrogenation (800–1000 psig) over nickel-cobalt-molybdenum on alumina catalyst, reported to be more efficient for nitrogen removal than cobalt-molybdenum.

PETROLEUM PROCESSING, Principles and Applications

Frontispiece. American Oil Co. refinery, Yorktown, Va. *(Petroleum Week.)*

Table 8-5. Typical Product Boiling Ranges

200-psig Operations (62)

	Feed	Products		Feed	Products		Feed	Product	Feed	Product
Octane, research, clear	36.5	85.0	95.0	51.0	85.0	95.0	43.4	95.0	29.6	85.0
Paraffins, %	49	....	....	34	....	....	59	....	65	
Naphthenes, %	43	....	....	43	....	....	28	....	19	
Aromatics, %	8	....	....	23	....	....	11	....	15	
10% off, °F	257	209	207	273	252	242	232	200	283	177
50% off, °F	291	285	288	306	303	298	260	258	310	270
90% off, °F	341	360	363	358	370	378	308	343	337	362
E.P., °F	373	448	457	385	437	455	336	390	355	419

275-psig Operations (11)

	Feed	Products		
Octane, research, clear	48.7	86.6	93.1	98.3
Paraffins, %	56	45	38	31
Naphthenes, %	41	1	0	0
Aromatics, %	12	52	60	68
10% off, °F	241	232	225	218
50% off, °F	260	265	267	268
90% off, °F	303	320	322	323
E.P., °F	332	365	374	373
RVP, lb	1.0	1.6	1.6	1.9

500-psig Operations (62)

	Feed	Products		Feed	Products		Feed	Products	
Octane, research, clear	36.5	85.0	95.0	51.0	85.0	95.0	43.4	85.0	95.0
Paraffins, %	49	....	....	34	....	....	59		
Naphthenes, %	43	....	....	43	....	....	28		
Aromatics, %	8	....	....	23	....	....	11		
10% off, °F	257	220	210	273	246	227	232	208	191
50% off, °F	291	286	281	306	298	291	260	261	256
90% off, °F	341	340	352	358	362	363	308	323	328
E.P., °F	373	414	420	385	432	440	336	378	387

Feed Preparation

As-produced feed stocks are sometimes not suitable for catalytic reformers, and feed-preparation operations may be required. The feed-preparation steps may consist of prefractionation, catalytic treatment to remove poisons, or both.

Prefractionation. Except where benzene is a primary product, materials lighter than heptanes do not make good feed stocks. No

Boiling Ranges

...s (62)

...d- ts	Feed	Prod- uct	Feed	Prod- uct
95.0	43.4	95.0	29.6	85.0
....	59	....	65	
....	28	....	19	
....	11	....	15	
242	232	200	283	177
298	260	258	310	270
378	308	343	337	362
455	336	390	355	419

...s (11)

Feed	Products		
48.7	86.6	93.1	98.3
56	45	38	31
41	1	0	0
12	52	60	68
241	232	225	218
260	265	267	268
303	320	322	323
332	365	374	373
1.0	1.6	1.6	1.9

...ns (62)

Feed	Products		Feed	Products	
51.0	85.0	95.0	43.4	85.0	95.0
34	...	...	59		
43	...	...	28		
23	...	...	11		
273	246	227	232	208	191
306	298	291	260	261	256
358	362	363	308	323	328
385	432	440	336	378	387

...ation

...mes not suitable for catalytic
...ns may be required. The feed-
...actionation, catalytic treatment

...nzene is a primary product,
...t make good feed stocks. No

aromatics are produced from pentanes, and little, if any, benzene is produced from hexanes under the conditions used commercially. Consequently, it is generally desirable to exclude materials lighter than heptanes from the reformer charge, and a prefractionation step to remove light ends is often included in the reforming plant.

Because aromatics are higher-boiling than the corresponding naphthenes or paraffins, aromatics produced from high-boiling components sometimes boil outside the range of gasoline and must be fractionated from the product. Aromatics outside the gasoline range are usually less valuable than the materials from which they were produced. Also, they tend to form coke on the reforming catalyst and thus deactivate it. For these two reasons, fractionation to remove heavy ends from the feed is often desirable, the end point of the feed being controlled so that the product has the proper end point without further fractionation.

In some refineries, the feed to reforming is fractionated into cuts of different boiling ranges (37), and each cut is reformed under the conditions optimum for it.

Pretreating. Catalytic treatment of feed stocks is required only for platinum catalysts, which are sensitive to certain trace elements, such as sulfur, nitrogen, water, chloride, lead, and arsenic (18,19,27). Sulfur, nitrogen, chlorides, and metals can be removed from the feed by mild hydrogenation, usually over a cobalt-molybdenum catalyst;* the hydrogen required is available, of course, from the reforming operation. Sulfur and lead are eliminated from some virgin naphthas by a bauxite pretreatment at high temperatures (6,14,52); and arsenic is taken out by passing the feed through a bed of clay at atmospheric temperature (48,52). Arsenic and lead can also be removed by acid treating (22).

Types of Units

Because increasing hydrogen pressures retard the production both of coke and of aromatics, two kinds of units may be designed. Units may be designed to operate at pressures high enough to permit long runs without regeneration (or with infrequent, off-stream regeneration), or they may be designed to operate at lower pressures with frequent, on-stream regenerations. The higher-pressure type is cheaper to build, but it is less flexible than the lower-pressure type, is limited in product octane number, and gives lower yields at comparable octane levels. The choice between the two must be made by balancing a lower investment cost on the one hand against a higher yield and greater flexibility on the other. Of the processes announced so far, five (Platforming, Catforming, Houdriforming, Sovaforming, and a Sinclair-Baker process) employ high pressures to ensure long on-stream periods. Because

* Hydrogen treating is discussed in Chap. 13.